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Ultra resolution chemical fingerprinting of dense non-aqueous phase liquids from manufactured gas plants by reversed phase comprehensive two-dimensional gas chromatography

Laura A. McGregor[a,*], Caroline Gauchotte-Lindsay[a], Niamh Nic Daéid[b], Russell Thomas[c], Paddy Daly[d], Robert M. Kalin[a]

[a] Department of Civil Engineering, University of Strathclyde, John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, UK
[b] Centre for Forensic Science, Department of Pure and Applied Chemistry, University of Strathclyde, Royal College Building, 204 George Street, Glasgow, UK
[c] Parsons Brinckerhoff, Queen Victoria House, Redland Hill, Bristol, UK
[d] National Grid, National Grid House, Warwick Technology Park, Gallows Hill, Warwick, UK

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ABSTRACT

Ultra resolution chemical fingerprinting of dense non-aqueous phase liquids (DNAPLs) from former manufactured gas plants (FMGPs) was investigated using comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry (GC × GC TOFMS). Reversed phase GC × GC (i.e. a polar primary column coupled to a non-polar secondary column) was found to significantly improve the separation of polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues. Sample extraction and cleanup was performed simultaneously using accelerated solvent extraction (ASE), with recovery rates between 76% and 97%, allowing fast, efficient extraction with minimal solvent consumption. Principal component analysis (PCA) of the GC × GC data was performed in an attempt to differentiate between twelve DNAPLs based on their chemical composition. Correlations were discovered between DNAPL composition and historic manufacturing processes used at different FMGP sites. Traditional chemical fingerprinting methods generally follow a tiered approach with sample analysis on several different instruments. We propose ultra resolution chemical fingerprinting as a fast, accurate and precise method of obtaining more chemical information than traditional tiered approaches while using only a single analytical technique.

1. Introduction

A dense non-aqueous phase liquid (DNAPL) is a liquid which is both heavier than water and immiscible in water [1]. In this case, DNAPL refers to coal tar; a common subsurface contaminant found at former manufactured gas plants (FMGPs). Coal tar DNAPLs are composed of thousands of organic and inorganic compounds, many of which may be found in trace quantities [2].

The complex chemical composition of DNAPLs has been shown to vary dramatically within a single FMGP site, as well as between different sites [3]. Accurate chemical fingerprinting is required at FMGP sites to ensure multiple sources of contamination are not present [4]. For example, more recent spills could be distinguished from historical gasworks contamination. Furthermore, for FMGPs split into multiple land holdings, accurate chemical fingerprinting can help to identify liability across the entire site. Given the large number of former gasworks sites in the U.K. and the introduction of recent "polluters pay" legislation, [5] it is reasonable to assume there may be many liability cases in the future, thus spurring the growth of the environmental forensics industry in the U.K.

Environmental forensic chemical fingerprinting of complex samples, such as coal tar and crude oil, is generally performed by gas chromatography (GC) in combination with either flame ionisation detection (GC–FID) or mass spectrometry (GC–MS) within a tiered analytical approach [4,6–8]. However, conventional GC techniques do not have the capacity to resolve the complex composition of coal tar DNAPLs [9]. Time-consuming and labour-intensive chemical fractionation processes are generally required to divide complex mixtures into several extracts prior to analysis [10].

There have been few reports on DNAPL composition in recent literature [3,11,12] and to the authors' knowledge there is no standardised approach for analysis of free phase coal tars, certainly not without extensive sample fractionation. Brown et al. [3] evaluated the composition of DNAPLs from ten different FMGP sites in the U.S.A indicating major differences in PAH composition between sites. However, this study utilised GC–MS analysis after lengthy

* Corresponding author. Tel.: +44 141 548 4773; fax: +44 141 553 2066.
E-mail address: l.a.mcgregor@strath.ac.uk (L.A. McGregor).

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fractionation processes, so the chemical information obtained on the DNAPLs was limited by resolution power of the technique. Generally, the literature focuses on challenges involved in characterisation and remediation of DNAPL contaminated land [2,13–15]. For example, Birak and Miller [2] state that full characterisation of DNAPLs at FMGP sites is still limited by analytical techniques. Utilisation of advanced chromatographic techniques for chemical fingerprinting of DNAPLs has thus been long-awaited to aid characterisation and allow the most effective remediation routes to be chosen.

Comprehensive two-dimensional gas chromatography (GC × GC) is a high-resolution separation technique, developed with the intention of overcoming limitations associated with conventional GC techniques [16]. The coupling of two columns with different selectivity allows for a two-dimensional separation of mixtures, across a retention plane rather than along a retention line [17–21]. An order of magnitude more compounds can be separated by GC × GC than when using conventional GC instrumentation [22].

Generally, a long, wide bore (0.25–0.32 mm i.d.), non-polar capillary column is used in the first separation, whereas a short, narrow bore (0.1–0.2 mm i.d.), polar column is installed for the second separation; this is deemed normal phase. However, reversing the column polarity has been shown to provide better group-type separation in certain cases [23]. The use of a polar, primary column and non-polar, secondary column is known as reversed phase (or reversed polarity) GC × GC [17].

GC × GC has been shown to be especially useful for environmental forensic analyses of complex samples [24,25]; the main advantage being the minimisation or elimination of fractionation processes prior to analysis [16,26]. A complex sample can be injected as a single extract to provide fast screening of the entire sample, allowing many classes of organic contaminants to be monitored at once. However, the technique has yet to be applied to the analysis of free phase coal tars.

This work aims to use GC × GC TOFMS to resolve the issues associated with the analysis and source apportionment of coal tar DNAPLs. Chemical fingerprinting of environmental samples by conventional GC techniques is described as a high resolution method. In this study, we demonstrate an enhanced method of chemical fingerprinting, deemed 'ultra resolution', by combining reversed phase GC × GC with statistical comparison using principal components analysis (PCA). This process gathers more chemical information per sample than traditional tiered approaches and has the additional benefits of using an efficient one-step extraction followed by analysis on a single analytical instrument.

2. Experimental

2.1. Samples and standards

DNAPL samples (labelled 1–12) were provided from seven different FMGP sites across the United Kingdom. The gas manufacturing processes used at each site are summarised in Table 1. DNAPL samples 1–6 were obtained from various locations within the same site (site A), while all other samples were acquired from different sites. Samples 1–10 were all obtained from sites that used coal retort stands for gas production, whereas sample 11 was obtained from a wood preservative site, where coal tar was distilled to produce creosote oil for coating wood [27]. Sample 12 was obtained from a carburetted water gas (CWG) plant where a mixture of hydrogen and carbon monoxide was produced by passing steam through heated coke rather than by the carbonisation of coal performed at retort gasworks [28]. The samples were stored at 4 °C prior to analysis.

Table 1
Description of FMGP sites.

Sample no.	Manufacturing process(es)	Sampling location
1	Vertical coal retort; potential traces of horizontal retort tar and gas oil (from micro-simplex gas reforming plant on site)	Borehole
2	"	Borehole near gas holder
3	"	Within tar tank
4	"	Within tar tank
5	"	Within tar tank
6	"	Borehole near tar tank
7	Horizontal coal retort	Base of gas holder
8	Horizontal coal retort	Within tar tank
9	Vertical coal retort; potential traces of carburetted water gas tar and horizontal retort tar	Unknown
10	Horizontal coal retort	Unknown
11	Wood preservation site; tar probably from a distilled fraction of creosote oil	Sump
12	Complex mixture of horizontal and vertical retorts, water gas and gas oil (from a gas reforming plant on site)	Borehole

All solvents used (*n*-hexane, dichloromethane) were of analytical grade, purchased from Fisher Scientific (Loughborough, U.K) and used without further purification. All deuterated PAHs were obtained from Isotec™, Sigma–Aldrich (Gillingham, U.K). All PAHs and alkylated naphthalenes were purchased from Sigma–Aldrich.

Anhydrous sodium sulphate, silica gel 60 (both from Sigma–Aldrich) and diatomaceous earth (Dionex, Camberley, UK) were activated for 4 h at 450 °C prior to use. Silica gel 60 was then deactivated by 10% water (w/w).

Alkylated naphthalenes were identified in the DNAPL extracts using individually prepared 200 μg/mL (in dichloromethane) standards of 1- and 2-methyl naphthalene and the 12 C2 alkyl naphthalene isomers.

Target analytes in the DNAPL extracts were quantified using calibration mixtures containing 16 PAHs, priority pollutants as listed by the U.S. EPA [29]. The 16 PAHs were purchased as a 2000 μg/mL stock solution in benzene:dichloromethane (1:1) from Sigma–Aldrich (Gillingham, U.K). A 2000 μg/mL stock surrogate solution containing deuterated PAHs (D8-naphthalene, D10-fluorene, D10-fluoranthene and D12-chrysene) was prepared to monitor extraction efficiency. Seven calibration standards containing the PAHs and surrogates were prepared within the concentration range of 2.5–500 μg/mL, each spiked with 75 μL of a 2000 μg/mL stock solution of D10-phenanthrene as an internal standard. Quantification was performed using the response of specific target ions present in GC × GC chromatograms (target ions are listed in Table S1 of supplementary data).

2.2. Sample preparation

Extraction was performed using an ASE 350 Accelerated Solvent Extraction system (Dionex, Camberley, UK) equipped with 10 mL stainless steel extraction cells. The high separation capability of GC × GC TOFMS eliminates the requirement for sample fractionation, thus a single extraction using hexane (including in-cell cleanup by silica gel) was performed.

A dry, homogeneous mix of DNAPL was prepared by grinding the DNAPL (approximately 0.5 g) with sodium sulphate ($NaSO_4$) and diatomaceous earth (D.E.) in a 1:1:1 ratio. This removes any water present in the DNAPL sample and results in a fine powder (rather than a tar) which can be transferred quantitatively to the

extraction cells. To ensure accurate quantification, the DNAPL was spiked with 600 μL of the surrogate solution prior to grinding with D.E. and $NaSO_4$. Any loss of target analytes could then be monitored from the start of sample preparation and storage of the sample in this form also allows any loss of target analytes over time to be monitored.

Extraction cells were lined with 2 filter papers (to ensure unwanted particulate matter did not collect in the extract) and packed with 3 g silica gel 60 (10% deactivated w/w). Approximately 0.5 g of the ground DNAPL/surrogate mixture was added to the extraction cell and the remaining cell volume was packed with D.E. Hexane was used as the extracting solvent for all extractions. ASE was performed at 150 °C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s were used. The extracts were concentrated to 1 mL using a Büchi Syncore® Analyst (Oldham, U.K). The extracts were then made up to exactly 10 mL using hexane. A 1 mL aliquot was then transferred to an autosampler vial and spiked with 75 μL of internal standard prior to analysis.

2.3. GC–MS analyses

A Thermo Scientific (Hertfordshire, U.K.) Trace Ultra GC fitted with a DSQII mass spectrometer and Triplus autosampler was used for all GC–MS analyses. The column was a J&W Scientific DB-5 fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). All injections were of one microlitre and were carried out using a split ratio of 1:50 and injection port temperature of 230 °C. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min. All standards and extracts were analysed with the oven temperature programmed at 10 °C/min from 55 °C (maintained for 2 min) to 110 °C, 3 °C/min to 210 °C, then at 8 °C/min to 320 °C (maintained for 15 min).

2.4. GC × GC TOFMS analyses

All GC × GC TOFMS analyses were performed using a Leco (St. Joseph, Michigan) time of flight mass spectrometer, model Pegasus 4D, connected to an Agilent 7890A gas chromatograph equipped with a Leco thermal modulator. The TOF ion source was fixed at 200 °C and masses between 45 and 500u were scanned at a 200 spectra/second rate. The detector voltage was set at 1700 V and the applied electron ionisation voltage was set at 70 eV.

All standards and extracts were analysed with the primary oven temperature programmed at 10 °C/min from 55 °C (maintained for 2 min) to 110 °C, 3 °C/min to 210 °C, then at 8 °C/min to 310 °C (maintained for 15 min). The secondary oven and modulator temperatures were programmed at a 20 °C offset relative to the primary oven. The modulation period was 6 s with a 1.3 s hot pulse time. The injection port temperature was set to 250 °C using a split ratio of 1:50. One microlitre of sample was injected for each run using an MPS2 twister autosampler (Gerstel). Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The normal phase column set comprised of a non-polar Rxi 5-Sil MS (25 m × 0.25 mm i.d. × 0.25 μm film thickness) primary column coupled to a mid-polarity Rxi 17 (1.2 m × 0.1 mm i.d. × 0.1 μm film thickness) secondary column, both supplied by Thames Restek (Buckinghamshire, U.K.). The reversed polarity column set comprised a mid-polarity TR-50 MS supplied by Thermo Scientific (30 m × 0.25 mm i.d. × 0.25 μm film thickness) as the primary column and a non-polar Rtx-5 supplied by Thames Restek (1.2 m × 0.18 mm i.d. m × 0.2 μm film thickness) as the secondary column, connected via a Thames Restek Press-tight® connector.

2.5. Principal component analysis

Variations in the DNAPL composition were evaluated by principal component analysis (PCA) using Minitab® 15 (Minitab Ltd., Coventry) software. Principal component analysis is a method used to extract the variations within a large data set by reducing raw sample data into smaller, uncorrelated variables known as principle components [30,31]. Score plots of the principal components which describe the most variation within the data allow relationships between the samples to be evaluated.

Peak areas of the tentatively identified compounds were imported into the statistical software after normalisation, against the peak area of the internal standard, and correction using the exact weight of DNAPL extracted for each sample.

3. Results and discussion

3.1. Optimisation of extraction procedure

The initial part of this study was dedicated to optimisation of extraction procedure, with the aim of extracting all chemical classes present in the DNAPL using a single Accelerated Solvent Extraction (ASE) method. Hexane was found to be a suitable extraction solvent, thus eliminating the need for harmful, chlorinated solvents. The ASE procedure utilised simultaneous extraction and clean-up, by the addition of silica gel to each extraction cell, thus further reducing the total analysis time and solvent consumption.

Fractionation of contaminated soil samples by ASE has previously been achieved by three separate extractions per cell using solvents of increasing polarity [32]. However, this was not possible for the DNAPL samples investigated in this study, as they were fully extracted by the initial, non-polar solvent despite attempts using low temperatures (40 °C) for the first extraction. GC–MS analysis of such complex samples would generally only be performed after chemical fractionation; however, given the ease of dissolution of the DNAPLs it is unlikely that effective fractionation could be achieved via ASE without the use of additional column chromatography. The high resolution capacity of GC × GC negates the requirement for sample fractionation thus the combination of sample extraction and cleanup by ASE provides fast screening of the entire coal tar composition.

Repeatability of the method was measured by extraction of six replicate cells, and subsequent GC–MS analysis, of DNAPL sample 7. Due to the difficulties involved in replicating a blank coal tar matrix, the surrogate recovery values were used as a measure of repeatability. Four deuterated PAHs (D8-naphthalene, D10-fluorene, D10-fluoranthene and D12-chrysene) were chosen as they span a range of molecular masses, from 136 g/mol to 240 g/mol. Recoveries between 76 and 97% were obtained based on the deuterated surrogate spikes. These values fall within the accepted range of 70–130% as stated by the U.S. EPA SW-846 Method 8000B [33]. Re-extraction of sample cells confirmed that the method provided exhaustive extraction of the DNAPL, with only the internal standard peak evident in the chromatograms of the second extracts. The relative standard deviation (RSD) of surrogate recovery was found to be below 10% for all deuterated surrogates, indicating satisfactory extraction repeatability.

3.2. Reversed polarity GC × GC

The column sets and GC × GC parameters were adjusted to achieve best possible separation of DNAPL components. Normal phase column sets are generally used in GC × GC analysis of environmental samples. Due to the restrictions in maximum operating temperature of most polar columns, a compromise generally exists

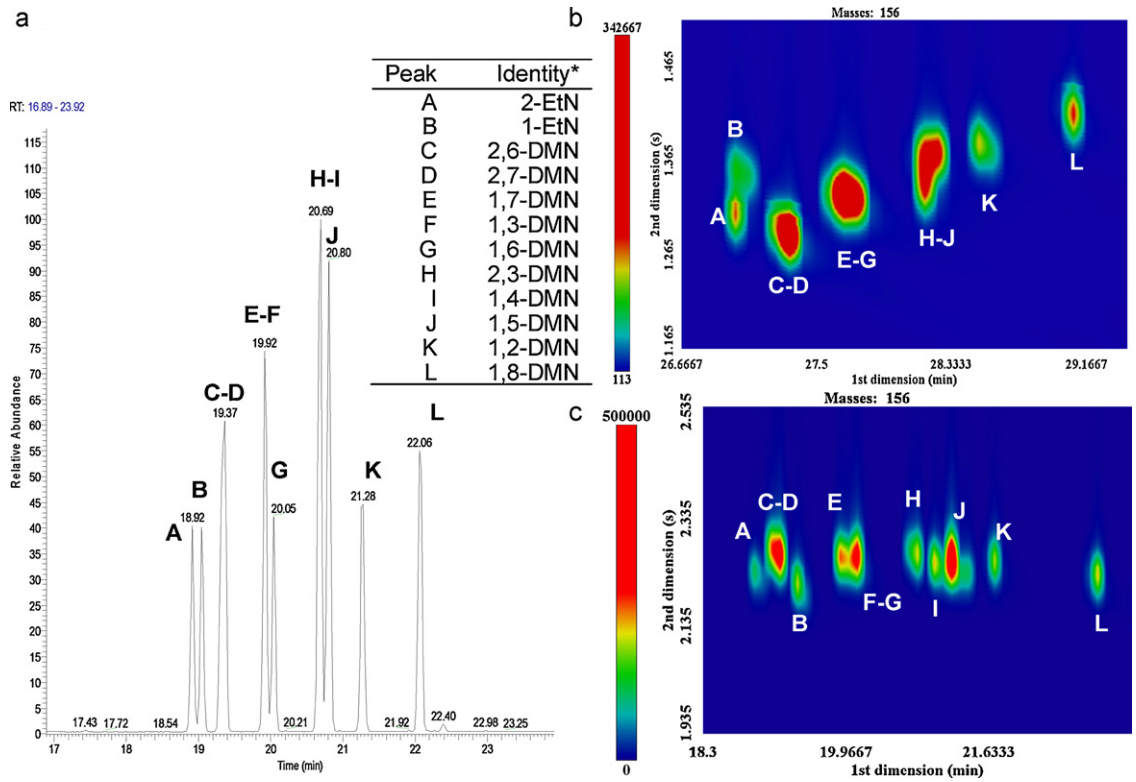

Fig. 1. Comparison of the separation capabilities of (a) GC–MS, (b) normal phase GC × GC and (c) reversed phase GC × GC using a standard mixture of C2 alkyl naphthalene isomers. The table provides the peak identities of the naphthalenes in each figure (*EtN = ethyl naphthalene, DMN = dimethyl naphthalene).

between column polarity and temperature programme for the secondary oven. The column phase was reversed to allow elution of the high molecular weight compounds present in DNAPLs while remaining within the limits of the column temperature range.

A standard mixture of C2 alkyl naphthalenes was used to confirm elution order and compare the separating power of three GC methods; GC–MS, normal phase GC × GC and reversed phase GC × GC. The C2 alkyl naphthalenes were chosen for this study as alkyl PAHs are often used in diagnostic ratios for source determination [7]. Due to insufficient separation with conventional GC techniques, the alkyl PAHs are generally combined by alkylation level, to provide diagnostic ratios based on quantification values for the group as a whole. For example, a typical diagnostic ratio using alkyl naphthalenes would be C0N/(C2N + C3N), where C0N is naphthalene and C2N and C3N are the C2 and C3 alkyl naphthalenes respectively [7]. We propose that the higher resolution of reversed phase GC × GC could allow enhanced diagnostic ratios to be calculated at no extra cost compared to normal phase GC × GC.

The chromatograms of the separation of a mixture of alkyl naphthalene isomers using GC–MS, normal phase GC × GC and reversed phase GC × GC are presented in Fig. 1. The GC × GC chromatograms are represented as contour plots; the *x*-axis represents the retention time in the primary column, the *y*-axis represents the retention time in the second column and the colour gradient represents the intensity of the peak. Normal phase GC × GC and GC–MS achieved separation of 7 and 9 peaks respectively. Reversed phase GC × GC allows separation of the 12 C2 alkyl naphthalenes into 10 peaks, with only 2 pairs of the alkyl naphthalenes still co-eluting (2,6- and 2,7-dimethyl naphthalene and 1,3- and 1,6-dimethyl naphthalene). Interestingly, normal phase GC × GC, which is generally used for the separation of complex samples, showed lower resolution for the alkyl naphthalenes than GC–MS.

The enhanced separation of reversed phase over normal phase GC × GC is further illustrated by chromatograms of the C3 and C4 alkyl naphthalenes (C3N and C4N respectively) in Fig. 2. Normal phase separates 9 peaks out of 34 possible C3N isomers and 14 of the 112 possible C4N isomers, while reversed phase separates 14 C3N and 20 C4N peaks within the same DNAPL sample. Full total ion chromatograms of DNAPL sample 1 by normal phase and reversed phase GC × GC TOFMS can be found in the supplementary data (Figs. S2 and S3 respectively).

The increased separation capacity of reversed phase is not only limited to alkyl PAHs. The DNAPL samples investigated in this study were found to contain a wide variety of chemical classes, including a range of alkylated heterocyclic PAH compounds. For example, alkyl benzothiophenes were abundant in all DNAPL samples. A comparison of the separating power of the two GC × GC modes for the benzothiophenes is shown in Fig. 3. The numbering indicates the peaks identified as alkyl benzothiophenes by their mass spectra, as some low intensity peaks can often be masked in the contour plot. Figs. 2 and 3 also illustrate the ordered structure of GC × GC contour plots; chemical families elute together in a band, allowing straightforward identification.

For example, the C1 alkyl naphthalenes elute together on a line with the higher alkylated homologues in subsequent bands. The structured layout of the contour plot allows peaks to be assigned quickly without the use of individual standards [34]. This form of tentative identification was used to assign the major chemical classes in the chromatogram of DNAPL 12 (Fig. 4) where the greatest variety of components was observed.

The 16 U.S. EPA priority PAHs are identified in Fig. 4, as well as their alkylated homologues. The elution order using reversed phase GC × GC is noticeably different to normal phase GC × GC. In normal phase, the alkanes and iso-alkanes elute before the PAHs in the second dimension due to their low affinity for the polar column. In reversed phase, the alkanes elute after the PAHs in the second dimension and are shown as a band along the top of the contour plot (Fig. 4).

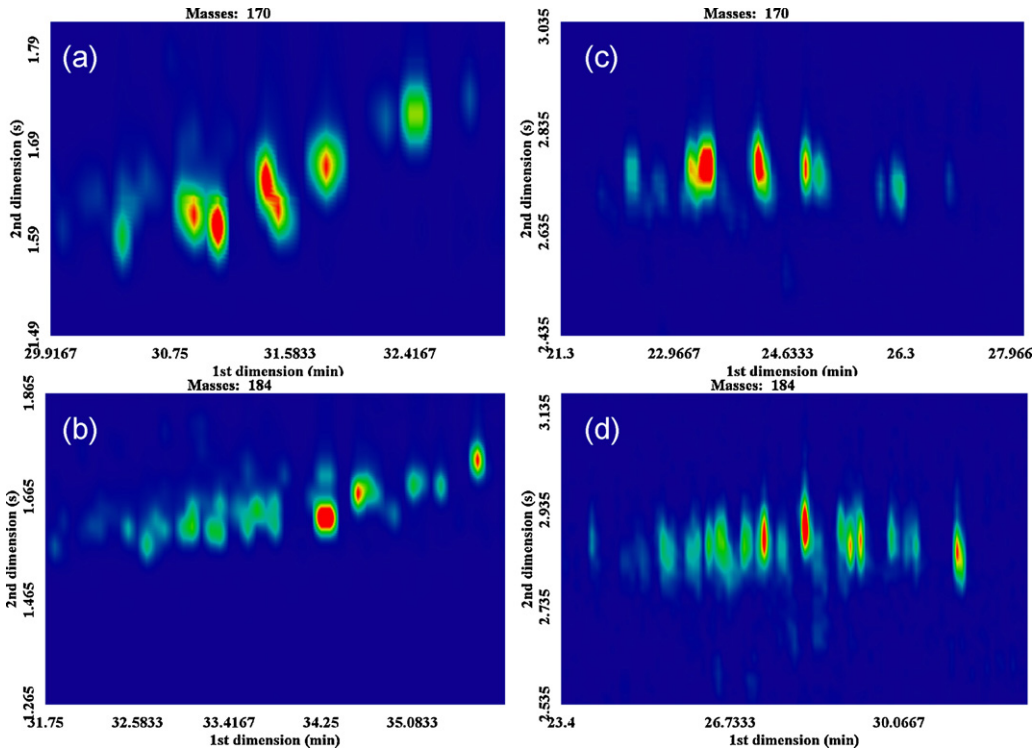

Fig. 2. GC × GC contour plots of C3 and C4 alkyl naphthalenes in DNAPL 1 using normal phase, (a) and (b) respectively, and reversed phase, (c) and (d) respectively.

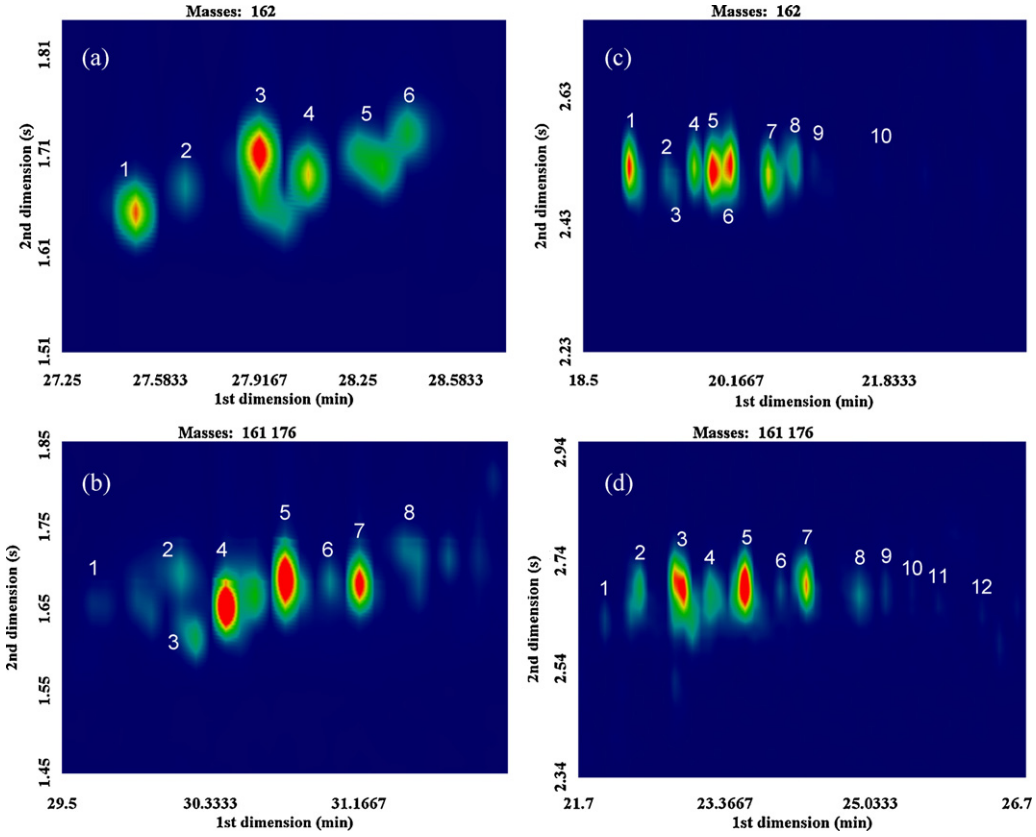

Fig. 3. GC × GC contour plots of C2 and C3 alkyl benzothiophenes in DNAPL 1 using normal phase, (a) and (b) respectively, and reversed phase, (c) and (d) respectively. Numbering indicates the peaks identified as alkyl benzothiophene isomers.

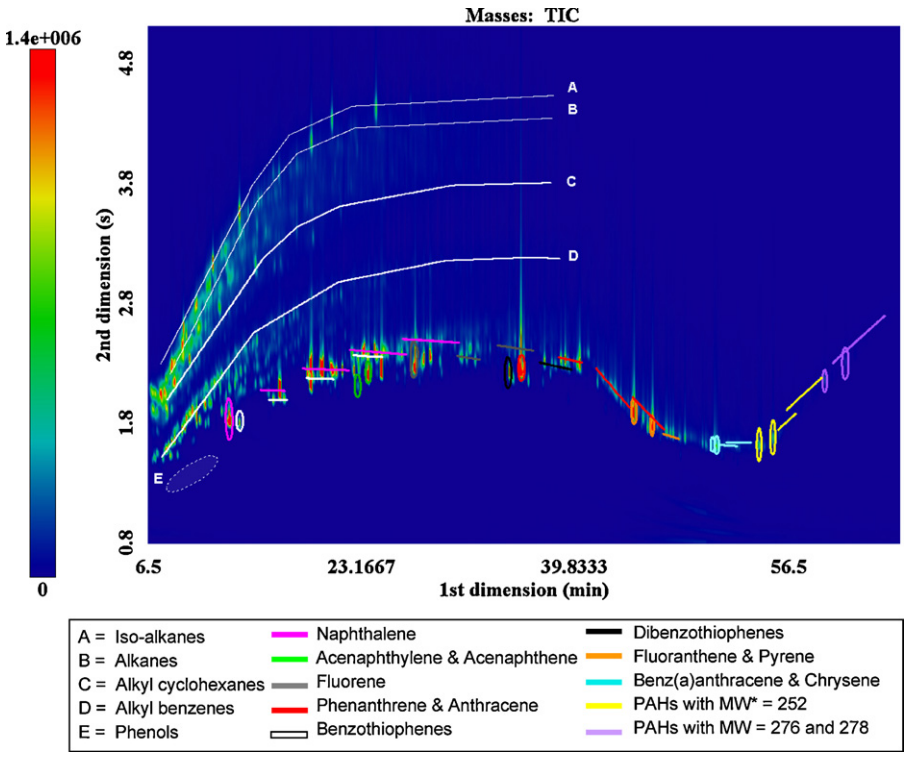

Fig. 4. GC × GC contour plot (in the total ion mode) of DNAPL 12. The key shows the identity of the compounds represented by each coloured circle. The solid lines of the same colour denote the alkylated derivatives of the corresponding compound [*MW = molecular weight].

3.3. PAH composition of DNAPLs

The 16 U.S. EPA priority PAHs were quantified using reversed phase GC × GC TOFMS. The PAH concentrations were corrected based on the percentage recovery values for the nearest eluting surrogate. The repeatability of the technique was evaluated by performing six identical injections of DNAPL sample 8. The average relative standard deviation (RSD) of the quantification was 3.0%, ranging from 0.3 to 4.8%. The low RSD values reflect the high separating power of GC × GC TOFMS.

Quantification was performed for the 16 EPA PAHs in all twelve DNAPL samples (Table 2). The majority of samples have very similar PAH fingerprints, with the same compounds being found in highest concentrations. Naphthalene was the most prevalent parent PAH in all DNAPLs except samples 11 and 12, where phenanthrene was found in highest concentrations. It is possible that this distinction is merely due to more advanced weathering in these samples (which will be discussed in more detail later).

Several PAH ratios were investigated as a simple method of comparing the DNAPL samples. The ratios used were Ant/(Ant + Phe), Flt/(Flt + Pyr) and BaA/(BaA + Chr), where Ant = anthracene, Phe = phenanthrene, Flt = fluoranthene, Pyr = pyrene, BaA = benz[a]anthracene and Chr = chrysene; the results are summarised in Table 3. These ratios have been used previously as a measure of pyrogenic/petrogenic character [35,36]. For pyrogenic samples, such as coal tar DNAPLs, Ant/(Ant + Phe), Flt/(Flt + Pyr) and BaA/(BaA + Chr) should give values greater than 0.10, 0.50 and 0.35 respectively [35,36]. However, for Flt/(Flt + Pyr) DNAPLs 1–5 produce values less than 0.50. Yunker et al. [36] state that values of 0.4–0.5 generally indicate combustion of liquid fossil fuel while values greater than 0.5 are indicative of solid fossil fuel combustion (e.g. coal). The unusual values for DNAPLs 1–5 could be explained by the presence of a gas reforming plant on site A, where petroleum fractions (instead of coal) were used to produce gas.

3.4. Chemical fingerprinting of DNAPLs

DNAPLs from different FMGP sites may differ widely in composition due to various factors involved in the manufacturing process. For example, different shapes of retort stand used to hold the coal during the carbonisation process will produce different by-products in the DNAPLs [28]. Similarly, low-temperature processes will produce DNAPLs containing a greater range of volatile components than high-temperature (>1000 °C) processes, as the higher temperatures tend to further degrade the volatile products [28].

However, PAH composition alone is not capable of differentiating between all seven FMGP sites. For the final part of this study, chemical fingerprints of the DNAPLs were produced by collating the peak data for a range of compounds, including aliphatics, alkylated PAHs and heterocyclic PAHs, using principal component analysis (PCA) for effective source differentiation.

Heterocyclic rings were the first group of chemicals to be explored, as compounds such as dibenzothiophenes are known to be resistant to environmental degradation processes and are used frequently for source identification of oil spills. GC × GC contour plots of the twelve DNAPLs allowed simple comparison of their chemical composition by visual inspection, allowing the major differences within the samples to be detected and investigated further using diagnostic ratio plots. A number of ratios were investigated using the peak areas (normalised to the internal standard) of carbazole (CBZ), dibenzofuran (DBF) and dibenzothiophene (DBT). The ratios CBZ/DBF and CBZ/DBT are represented as a cross plot in Fig. 5. The plot shows that the ratios can effectively separate the major types of manufacturing process, but are not capable of discerning between smaller differences, such as retort shape. The low CBZ/DBT values of sites containing a reforming gas plant may be due to the presence of petroleum fractions which would most likely contain high levels of dibenzothiophene with respect to carbazole.

Principal component analysis (PCA) was then performed to compare the chemical compositions of the twelve DNAPLs in an attempt

Table 2
PAH composition of DNAPLs (units are in mg/kg).

Compounds	DNAPL											
	1	2	3	4	5	6	7	8	9	10	11	12
Naphthalene	16,797	9867	4617	5788	1068	481	47,171	85,432	31,763	81,931	36,169	4222
Acenaphthylene	4206	3891	1605	1857	503	252	8309	16,567	5044	7131	2333	924
Acenaphthene	883	407	244	252	93	57	1365	1485	1455	1538	22,458	6678
Fluorene	1917	1334	774	832	267	122	5612	6970	3644	5251	15,764	6877
Phenanthrene	3341	2730	1743	1930	567	271	21,304	29,445	10,892	20,107	36,896	11,361
Anthracene	3511	1308	945	984	437	235	11,298	7194	7180	8982	15,630	7774
Fluoranthene	1773	860	962	975	269	223	16,589	13,630	9220	14,988	10,518	8157
Pyrene	2079	1414	1074	1076	292	216	14,526	11,821	7165	12,844	7926	6141
Benz[a]anthracene	688	441	372	416	103	84	6763	5184	3265	5538	2228	4904
Chrysene	710	388	326	348	59	46	6674	4759	3706	5307	2447	4426
Benzo[b]fluoranthene	45	79	77	117	11	16	3187	1957	1656	2990	663	2472
Benzo[k]fluoranthene	306	174	170	226	45	32	4855	6408	2543	4362	828	2894
Benzo[a]pyrene	3282	1046	899	917	363	267	15,367	18,823	11,506	15,016	3137	3371
Indeno[1,2,3-cd]pyrene	42	83	43	79	13	13	2303	2133	1010	2165	306	1395
Dibenz[a,h]anthracene	196	48	23	29	15	14	606	913	490	600	62	868
Benzo[g,h,i]perylene	272	62	55	78	32	26	2263	2183	1271	2168	371	1332

Table 3

DNAPL	Ant/(Ant + Phe)	Flt/(Flt + Pyr)	BaA/(BaA + Chr)
1	0.51	0.46	0.49
2	0.32	0.38	0.53
3	0.35	0.47	0.53
4	0.34	0.48	0.54
5	0.44	0.48	0.64
6	0.46	0.51	0.65
7	0.35	0.53	0.50
8	0.20	0.54	0.52
9	0.40	0.56	0.47
10	0.31	0.54	0.51
11	0.30	0.57	0.48
12	0.41	0.57	0.53

to fully differentiate between the manufacturing processes used at the seven FMGP sites. In total, the data for 140 peaks was entered into the software, including PAHs and their alkyl homologues, alkanes, alkyl benzenes and a range of heterocyclic PAH compounds, resulting in the PCA score plot shown in Fig. 6a. A full list of the compounds used to prepare each score plot has been included in the supplementary information (Table S1). The inclusion of peak areas for individual alkylated PAHs and heterocyclic PAHs provides 77 more data points per sample than if groupings by alkylation level were used, as in conventional chemical fingerprinting methods.

The first two principal components in Fig. 6a describe 78.5% of the total variation in the data set. The score plot illustrates that it is possible to distinguish between the FMGP sites based on DNAPL composition. DNAPLs 1–6 originate from the same FMGP site (site A) and are shown to be very similar in nature as they form a cluster in the score plot. This indicates that the peak data used to prepare the score plot provides a good source fingerprint for the DNAPL samples. Samples 1–6 are clustered in a separate quadrant to the other coal retort DNAPLs. It is hypothesised that the variety of processes used at site A has resulted in a complex mix of coal retort tar and reforming gas plant contamination.

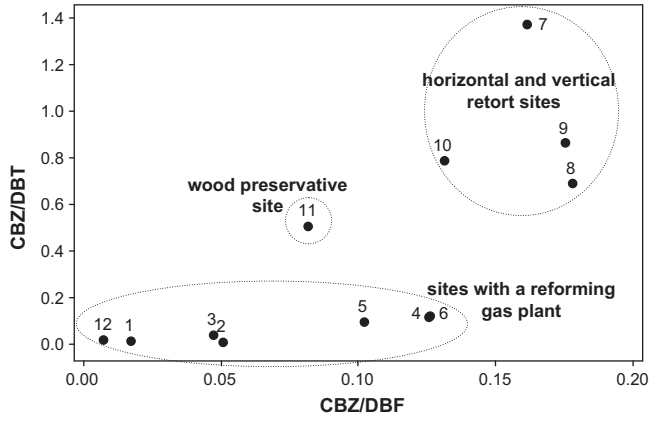

Fig. 5. Cross plot of heterocyclic ratios using carbazole (CBZ), dibenzofuran (DBF) and dibenzothiophene (DBT) for source apportionment.

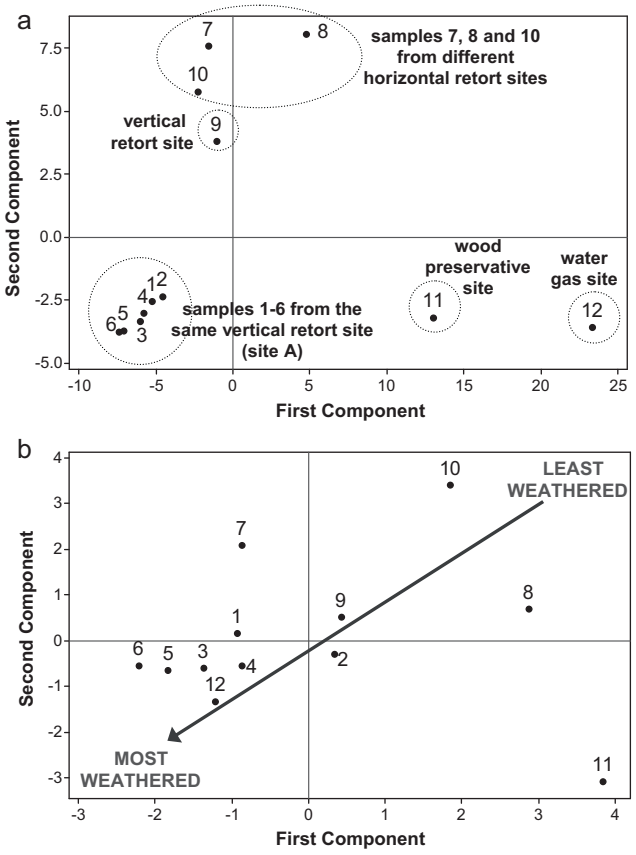

Fig. 6. Principal component analysis (PCA) score plots comparing peak areas of (a) 140 different components* and (b) compounds susceptible to weathering, found in twelve DNAPL samples (labelled 1–12) from seven different FMGP sites. [*a full list of compounds used to prepare each plot can be found in Table S1 of the supplementary information].

Horizontal and vertical retorts create different by-products as their different shapes cause the gases evolved during the carbonisation of coal to be kept in contact with the hot walls of the retort for different lengths of time. Previous literature states that DNAPLs produced by a horizontal retort will be rich in phenol and naphthalene [28], most likely due to the increased contact time with the retort walls allowing the higher molecular weight PAHs to be degraded. Sample 8 appears in a different quartile of the score plot to the other horizontal retort DNAPLs (samples 7 and 10). This sample was obtained from inside a tar tank, thus it is likely that the differences in chemical composition may be due to a lower extent of weathering than in the other samples.

As expected, DNAPL samples 11 and 12 showed a high degree of difference from the other samples as they originated from a wood preservative site and water gas site respectively, whereas all other samples were obtained from horizontal or vertical retort coal gasworks. The DNAPL found at a wood preservative site is most likely to be from creosote oil, a distilled fraction of coal tar DNAPLs which was used to treat wood [28]; hence samples from such sites will likely exhibit a smaller range of compounds than those obtained from water gas and coal retort sites. Alkane peak areas were included in this plot as previous literature [28] states that they are more prevalent in DNAPLs from water gas sites, allowing sample 12 to be easily distinguished from the other DNAPLs.

3.5. Weathering of DNAPLs

The use of a wide variety of compounds in the initial PCA score plot (Fig. 6a) provided a chemical fingerprint able to distinguish between different DNAPL sources. A further PCA score plot was prepared in an attempt to differentiate between the samples based on the degree of weathering present (Fig. 6b). The 'weathering plot' incorporates a number of weathering ratios calculated for each DNAPL and the peak areas of low molecular weight compounds which are most susceptible to weathering. A weathering ratio for alkanes, using the peak areas of the straight chain alkanes (or n-alkanes) divided by the peak areas of the branched alkanes, was included to ensure the large differences in alkane concentrations caused by different manufacturing processes was not an issue. The values for a PAH weathering ratio, calculated based on the total C2 and C3 alkyl naphthalenes (C2N and C3N respectively) compared to naphthalene (C0N) itself, C0N/(C2N + C3N), was also included due to the tendency for alkyl homologues to be more prevalent in severely weathered samples.[7] Furthermore, an equivalent ratio for the benzothiophenes (one of the most prevalent heterocyclic families found in the DNAPLs) was also included. The calculated ratios for each sample are given in the supplementary information (Table S4).

The first two principal components in the weathering plot describe 82.5% of the total variation. Samples 1–6 show a more pronounced difference in this plot compared to the initial score plot in Fig. 6a. This demonstrates that the there is a degree of difference in their chemical fingerprints which may be attributed to different weathering processes occurring across the site. Samples 1 and 2 were obtained from boreholes in a similar area at site A, whereas samples 3–5 were all obtained from within a tar tank near the site boundary and sample 6 was obtained from a borehole next to the same tar tank. This is illustrated in the weathering plot, as samples 1 and 2 have separated from the cluster of other samples obtained from site A.

By inspection of the peak areas and ratios used to prepare the PCA plot in Fig. 6b, a trend in the degree of weathering can be approximated; samples in the top-right quartile appear to show less severe weathering, while those towards the bottom-left quartile indicate the most severe cases of weathering. The degree of weathering in samples 11 and 12 was evaluated by inspection of the concentrations of alkyl PAHs relative to the parent PAH. The concentration of PAHs and their homologues in the majority of samples display the expected pyrogenic PAH pattern, C0 > C1 > C2 > C3, signifying that these samples have not undergone significant weathering [37]. However, in samples 11 and 12 (and to a slightly lesser extent in samples 5 and 6) the concentrations are more similar to the accepted weathering pattern of C0 < C1 < C2 < C3, indicating that these samples are more severely weathered. An illustration of the weathering patterns of naphthalenes and benzothiophenes in each of the DNAPL samples can be found in the supplementary information (Figs. S5 and S6).

PCA plots have been shown to be capable of not only distinguishing between DNAPLs from different types of FMGP sites, but the degree of weathering can also be estimated by exclusion of the more stable compounds generally used as source indicators. This analytical process could prove very useful in distinguishing the differences between DNAPLs caused by differences in the manufacturing processes employed at FMGP sites, as well as in distinguishing differences in chemical fingerprint across a single FMGP site. As previously mentioned, many FMGP sites have now been split into various land holdings and PCA plots of GC × GC data from across the entire site may help to indicate the presence of multiple sources of contamination, thus determining the persons liable for remediation costs. The reasons for variation of chemical fingerprint across a site, e.g. environmental weathering or multiple contamination sources, can be confirmed using ancillary methods, such as CSIA. The combination of reversed phase GC × GC with PCA outlined in this study allows large amounts of chemical information to be generated for each sample but collated in a manageable format. It is for this reason that we deem this method of chemical fingerprinting as "ultra resolution".

4. Conclusions

This study details the first attempt at development of a standard approach to chemical fingerprinting of coal tar DNAPLs. Conventional tiered approaches to chemical fingerprinting involve tedious sample preparation and cleanup steps, multiple analytical instruments and complicated data processing. The use of reversed phase GC × GC TOFMS provides an accurate and precise method of chemical fingerprinting for complex samples, such as coal tar, by analysis of a single, non-specific sample extract using a single analytical instrument. The application of principal component analysis to sections of the GC × GC dataset has been shown to simplify the comparison of highly complex samples. PCA score plots can be used to compare the chemical fingerprints of a number of samples at once, allowing site-specific differences to be easily identified. The method described could prove particularly useful for source identification and monitoring of natural attenuation during environmental forensic investigations at former gasworks and at a multitude of other contaminated sites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.05.045.

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